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a study on well defined Platinum Nano-Clusters

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Fuel Cell Catalyst degradation mechanisms

a study on well defined Platinum Nano-Clusters

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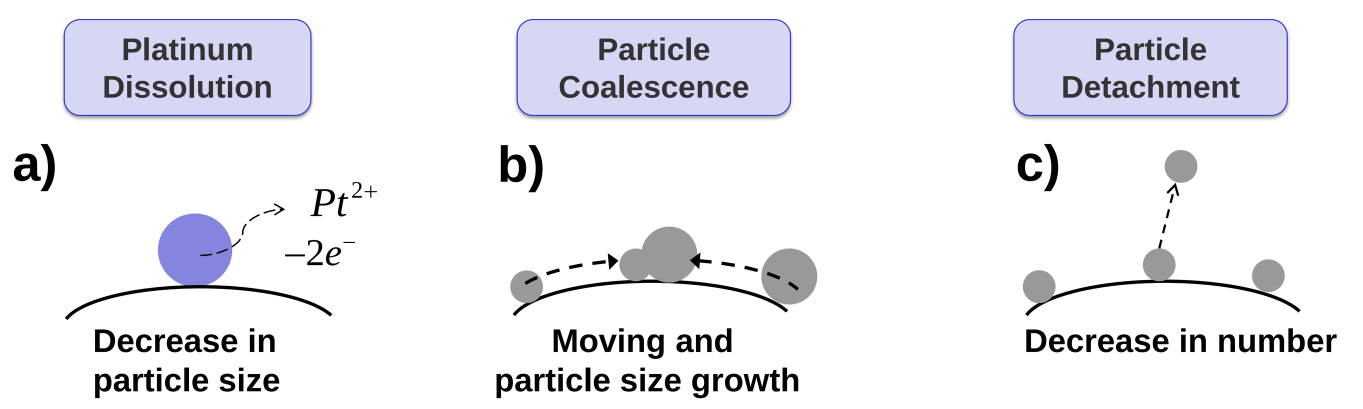
2 D Model system: easier to study & without the influence of the support

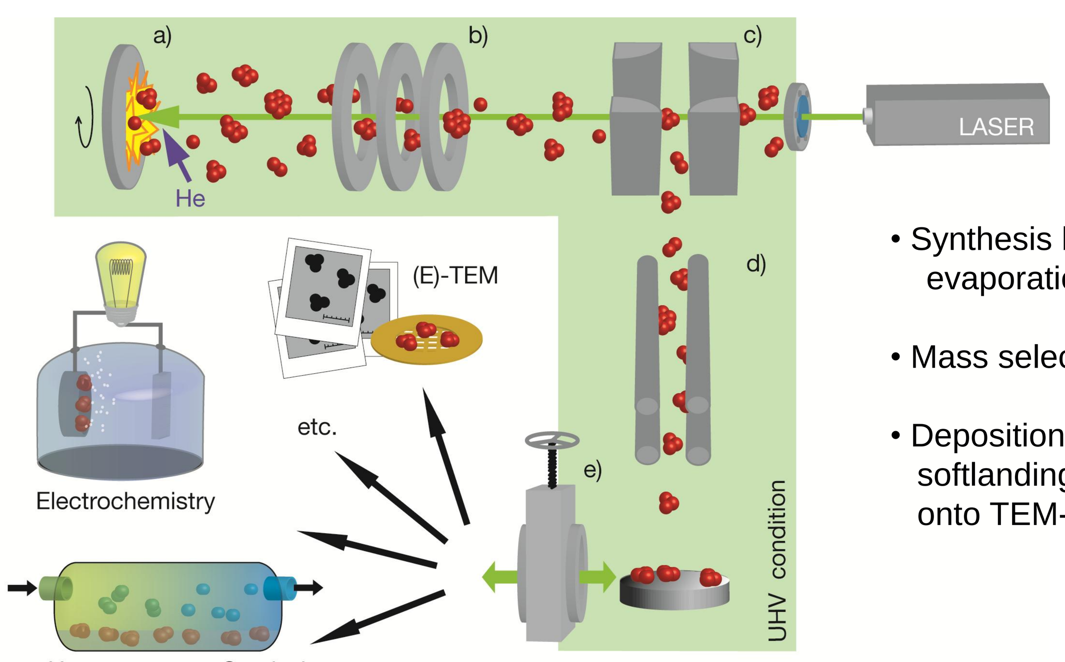


One of the main fundamental problems of polymer electrolyte membrane fuel cells (PEMFCs) to date is a low practical efficiency, due to the degradation of the catalyst in a fuel cell during operation. Especially to clarify the ongoing processes and the responsible factors for the degradation and therefore the loss of usable catalytic active material, is one important step to achieve long term stability of PEMFCs.

In this study we used Pt-Nanoclusters (NCs) supported on TEM gold grids as a model system for Fuel Cell Catalysts to address the widely discussed mechanisms of Fuel Cell Catalyst degradation. Accelerated aging tests with different potential profiles are used to study the main responsible degradation mechanism.

Experimental Setup

Deposition of Pt cluster catalyst under UHV. [1]

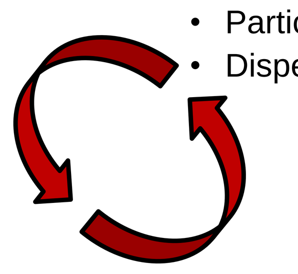


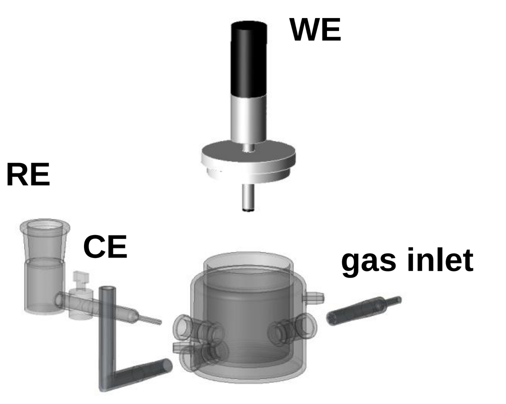
- Synthesis by laser evaporation
- Mass selection by QMS
- Deposition under softlanding conditions onto TEM-Grids

(Scanning) Transmission Electron Microscopy

- Particle structure and size
- Dispersion on the carbon support

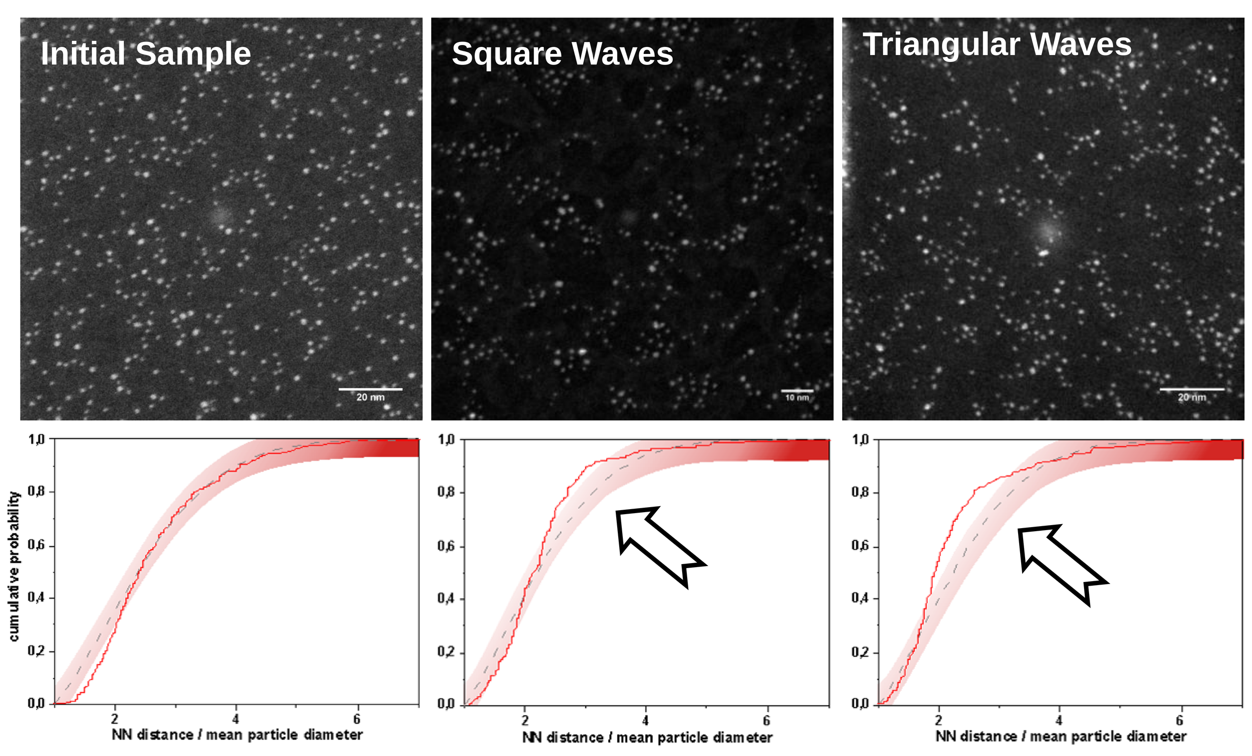
Accelerated degradation tests





- three electrode setup with home build all-Teflon electrochemical cells.
- the measurements are automated using in-house written Labview software controlling the RDE, gas changers and a home build potentiostat.

Particle Distribution



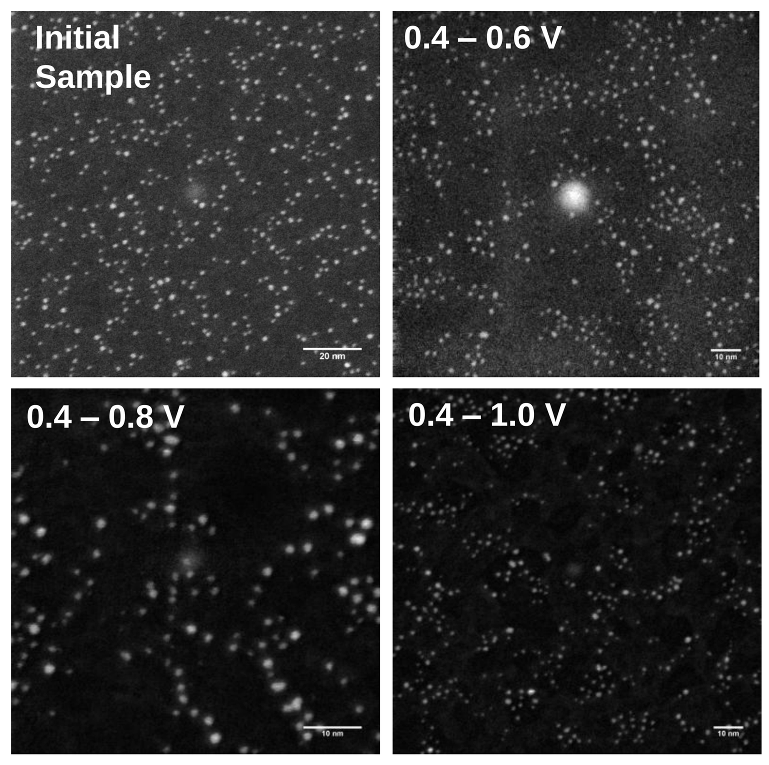
- STEM images were taken from the cluster samples before and after accelerated aging tests.
- Statistical analysis of the nearest neighbour distribution shows clear differences in the nanocluster distribution on the carbon film.

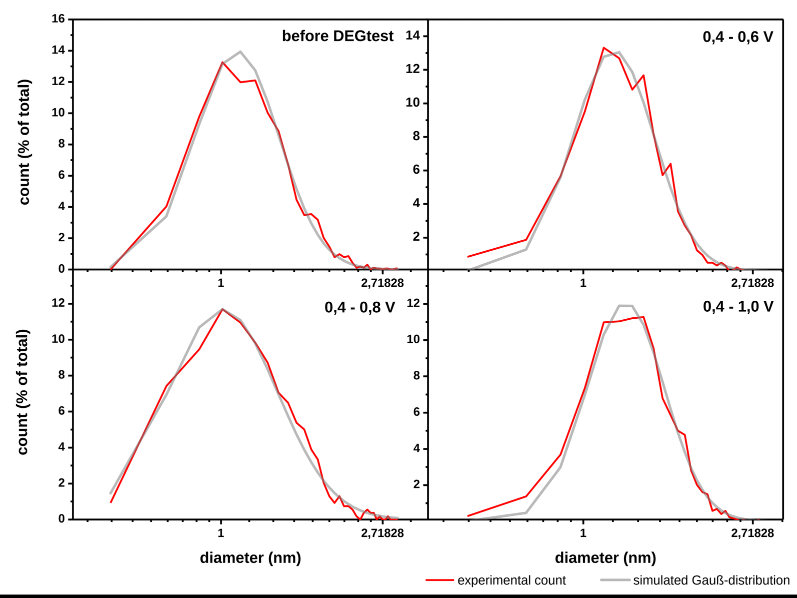
Initial Sample – the cumulative probability of the clusters (red line) is in good agreement with the theoretical curve assuming a random distribution (gray dashed line) [2] (red colored region displays a statistical significance of 5%)

after Degradation-test - the NN distance distribution after 3000 Square Waves (0.4 – 1.0 V, 3s:3s) or 4 hours triangular waves (0.4 – 1.0 V, 250 mV/s) deviates in the region of 2 – 3.5 times the average nanocluster diameter from the theoretical curve.

- **Clusters moved during the aging tests**
- **loss of random distribution**
- **favoured distance between 2 and 3.5 times the average diameter**

Square Waves



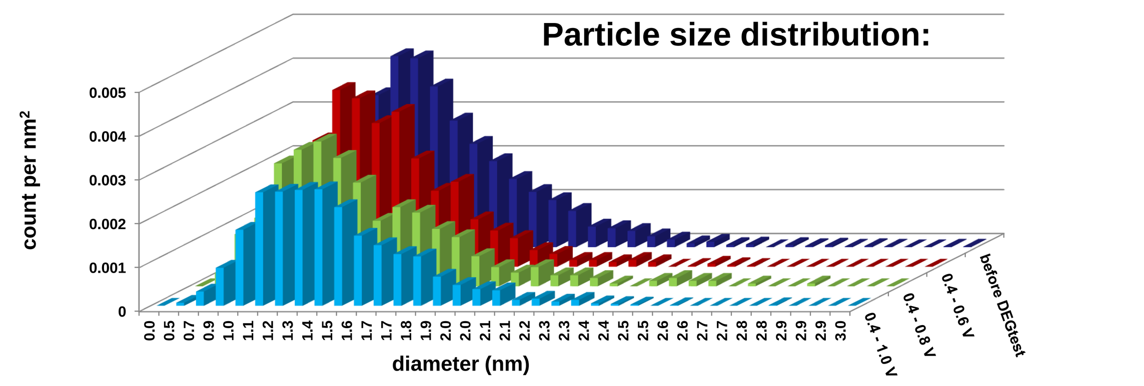


Particle size distribution depending on the potential window:

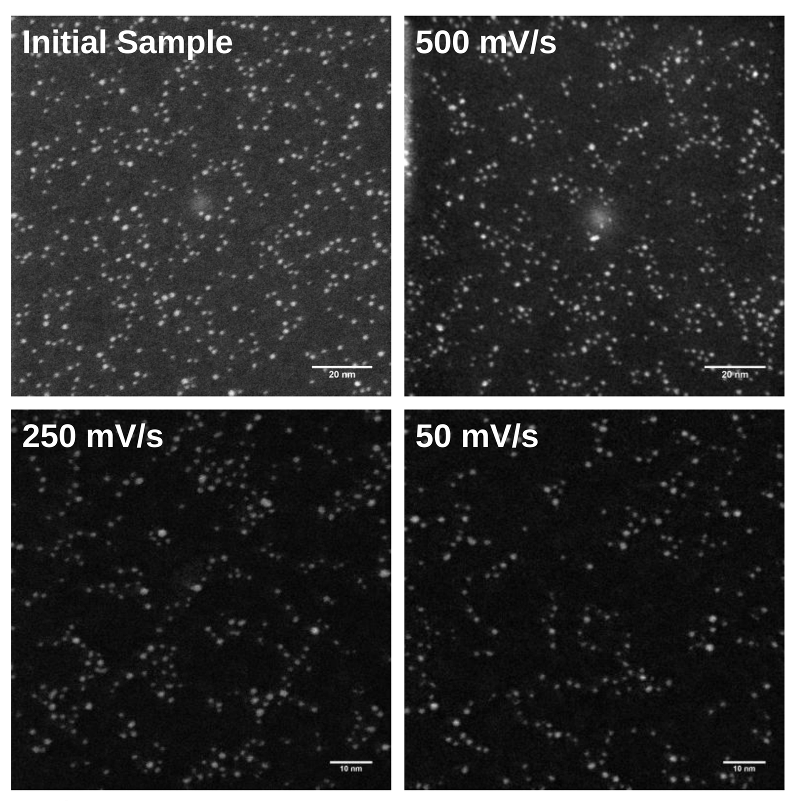
- total number of particles decreases significantly when using the largest potential window, while the range of cluster sizes stays constant
  - high losses especially for smaller particles
- no growth of particles could be detected
- the shape of the particle size distribution stays unchanged before and after the aging tests, independent from the potential window
  - The log-normal distribution of the cluster diameters (red curve) shows for all samples a gaussian (gray line for simulated distribution), indicating the absence of Ostwald Ripening [3] in case of a square wave potential profile.
- **no coalescence due to agglomeration**
- **no Ostwald Ripening**
- **most likely simple particle detachment from the support**

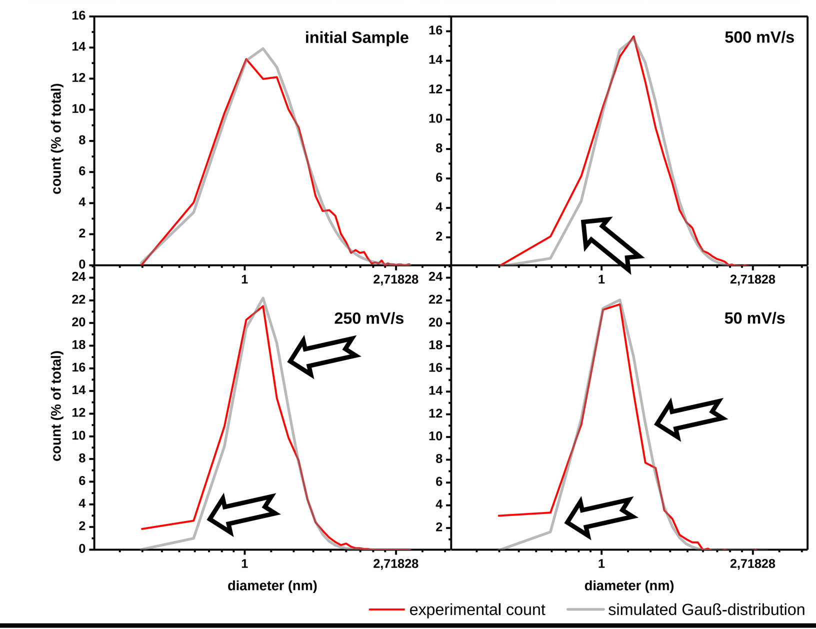
Sample	Initial Sample	0.4 – 0.6 V	0.4 – 0.8 V	0.4 – 1.0 V
Cluster / nm²	0,036	0,031	0,034	0,021
Av. Diameter (nm)	1,33	1,35	1,33	1,46

Particle size distribution:



Triangular Waves



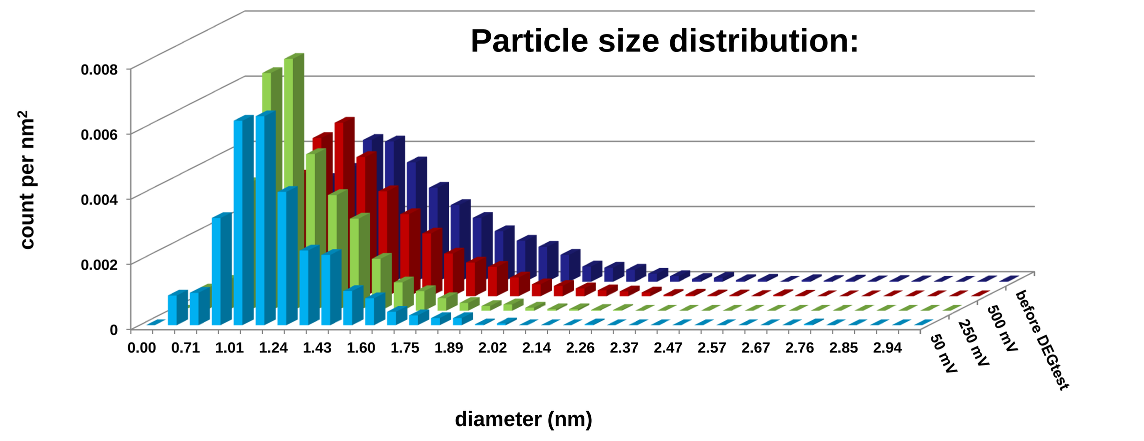


Particle size distribution depending on the scan rate:

- total number of particles decreases only slightly when the slowest scan rate is used, while the average diameter decreases constantly with decreasing scan rate
- number of large particles decreases
- the size distribution shifts to smaller diameter with a narrow, nearly normal curve distribution.
  - The log-normal distribution of the cluster diameters (red curve) deviates from the ideal Gaussian curve, particularly at small diameters.
- **slow scan rates are most effective**
- **no coalescence due to agglomeration**
- **no simple particle detachment but reshaping of the clusters**

Sample	Initial Sample	500 mV/s	250 mV/s	50 mV/s
Cluster / nm²	0,036	0,036	0,036	0,029
Av. Diameter (nm)	1,33	1,33	1,15	1,13

Particle size distribution:



Acknowledgements:
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[1] U. Heiz, et. al, *Rev. Sci. Instrum*, ***1997***, *68*, 1986.
[2] S. Torquato, B. Lu, J. Rubinstein, *Phys. Rev. A*, ***1990***, *41*, 2059.
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